United States Environmental Protection Agency **Office of Research and Development**

National Exposure Research Laboratory
Research Abstract
Government Performance Results Act Goal: Clean Air

Significant Research Findings:

Atmospheric Chemistry of Mercury Compounds

Scientific Problem and Policy Issues

A full assessment of the atmospheric release of compounds listed in the EPA Urban Air Toxics Strategy requires high quality chemical mechanisms that can be used to determine atmospheric lifetimes and fates. This information is needed to predict (1) ambient concentrations that affect human exposure levels and (2) dry and wet deposition rates that control uptakes of compounds to ecologically sensitive land surfaces and aquatic bodies and potentially lead to indirect human exposures through ingestion. To address this issue the U.S. Environmental Protection Agency (EPA) has designed a research program to develop the necessary information to construct chemical mechanisms for air toxic compounds. The first stage of the program that began in FY01 consists of conducting a critical literature review of the atmospheric chemistry of air toxic compounds. The results will be used (1) to identify research required to fill in gaps and reduce uncertainties in the chemical mechanisms and (2) to produce, where possible, literature-based chemical mechanisms. The first set of compounds to be evaluated are inorganic mercury (Hg) compounds. Volatile inorganic Hg compounds are emitted into the atmosphere mainly as elemental mercury (Hg^0) and to a lesser extent as oxidized compounds (Hg^{II}). Once emitted Hg^0 may react with atmospheric free radicals to form Hg^{II} compounds that readily deposit by dry and wet processes to land and aquatic surfaces. Deposited Hg compounds can be transformed by natural biological compounds into toxic methyl mercury that is bio-concentrated in the aquatic food chain more than a million fold. Human consumption of Hg-contaminated marine and fresh water fish can lead to significant adverse health effects from (1) transport of methyl mercury to the brain through the blood-brain barrier and (2) penetration into the placenta. The chemical mechanistic data gathered under this research program will be used to develop chemical mechanisms for air quality models that will be used by EPA and States to help characterize risk from and evaluate control strategies for Hg compounds.

Research Approach

A review of the peer reviewed literature will be undertaken to assess the state of science of atmospheric chemistry of inorganic Hg compounds. The review includes (1) evaluating rate constants for gas phase reactions of Hg^0 with reactive gas phase constituents including O_3, OH, Cl and NO_3; (2) determining the extent to which oxidation products of such reactions have been identified; (3) assessing similar rate constant and product data for reactions of dissolved Hg and Hg^{II} compounds in aqueous media including fog water and cloud water; (4) evaluating the status of equilibrium constants for aqueous reactions between the Hg^{2+} and atmospherically relevant anions including Cl^-, OH^-, and SO_3^{2-}; (5)

assessing the extent to which Hg compounds partition between the gas and aerosol phases. Based on the literature review, recommendations for what should be included in a chemical mechanism for inorganic Hg compounds are presented along with a list of research recommendations for filling gaps and reducing uncertainties in the mechanisms.

Results and Implications

Results of the literature review reveal that significant uncertainties and gaps remain in our understanding of the atmospheric chemistry of inorganic Hg compounds. The atmospheric chemistry of Hg compounds is highly complex, far more complicated than that of hydrocarbons involved in smog formation, a major focus of the EPA's model development efforts over the past 30 years. Both Hg^0 and Hg^{II} compounds are reactive, semivolatile, water-soluble compounds that can partition between the gas and aerosol phases and between the gas phase and atmospheric aqueous phases, including cloud water and fog water. In addition to undergoing gas phase reactions, Hg compounds, upon dissolution into aqueous media, are subject to a complex series of reactions with a variety of oxidizing and reducing agents. To date only a limited number of laboratory investigations have been carried out to investigate these chemical processes. Based on these data chemical mechanisms have been developed for predicting ambient Hg concentrations. The complexities of the proposed chemical mechanisms range from simple mechanisms up to multi-phase mechanisms that include gas phase reactions, gas-aerosol phase partitioning, partitioning between the gas phase and ambient aqueous media including cloud water and fog water, and aqueous reactions involving dissolved Hg compounds. While existing models are important first generation tools for evaluating Hg control strategies and characterizing the potential risks from Hg exposure, the proposed chemical mechanisms remain largely unevaluated and gaps and uncertainties remain in the parameterizations of key chemical processes.

The literature review revealed a number of significant uncertainties and gaps in the gas phase chemistry. To date the gas phase reactions of O_3 and OH with Hg^0 are the most studied Hg gas phase reactions, although even for these compounds there are considerable uncertainties in the rate constant measurements and there are no direct measurements of the oxidation products. There are no rate constant measurements or product studies for the reactions of Hg^0 with other oxidants including HO_2 and Cl. For this reason the gas phase atmospheric lifetime of Hg^0, an important parameter in air quality models, remains uncertain. The aqueous chemistry, while highly complex, is better understood than gas phase chemistry. Hg compounds are taken up into aqueous media, including cloud water and fog water, where they can be oxidized to Hg^{II} compounds, some of which may be volatile and can be released into the atmosphere. On the other hand, dissolved Hg^{II} compounds are subject to reactions with reductants, among them HO_2 radicals, forming Hg^0 that can be released into the atmosphere. While many aqueous Hg reactions have been studied individually, there have been no investigations of Hg reactions in aqueous media of the chemical diversity of ambient cloud water, fog water, and precipitation samples that include a wide range of dissolved reactive molecules as well as many ionic complexes, some of which

are solids. Finally, the interaction of Hg compounds with ambient aerosols has only very recently been addressed, and significant uncertainties in the parameterization of the partitioning mechanism between the gas and aerosol phases remain.

Based on this review of the literature, a set of guidelines are provided that describe the chemical processes that should be included in a chemical mechanism for inorganic Hg compounds. A number of published chemical mechanisms include many of these processes and may be sufficient to *estimate* ambient gas phase Hg^0 concentrations. However, additional laboratory studies are required to develop high quality chemical mechanisms for accurately predicting ambient concentrations of Hg^0 and Hg^{II} in both the gas and aerosol phases as well as in cloud water, fog water, and precipitation. To address this issue, a set of research recommendations are presented.

This research project directly supports ORD's research to improve the scientific foundation of human health risk assessment under the Government Performance and Results Act (GPRA) Goal 1: Clean Air; Objective 2: Eliminate Risks from Air Toxics; Sub-Objective 1: Conduct Air Toxics Research. The results of this project address GPRA annual performance goal (APG) 06: In Fiscal Year 2000, develop an air quality model incorporating (1) air toxics as their chemistry and emissions become known and (2) source emissions and control information for both mobile and stationary sources to guide cost-effective risk management.

Research Collaboration and Publications

The review of the atmospheric chemistry of inorganic Hg compounds was conducted by a National Exposure Research Laboratory staff scientist. This research findings will be presented at several conferences and are contained in the following manuscript:

Edney, EO. "Atmospheric Chemistry of Inorganic Mercury Compounds." *Journal of Air and Waste Management Association*. (Submitted in 2001.)

Future Research

Future research will include the development of a research program for carrying out laboratory chemistry studies to fill in gaps and reduce uncertainties in the atmospheric chemistry of Hg compounds.

Contacts for Additional Information

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